12.8 Sieve the dried sample through a 60-mesh sieve for 10 minutes using a mechanical shaking device.

12.9 Transfer the soil passing through the 60-mesh sieve to the pre-weighed plastic vial labeled Fine. Weigh the combined (vial + sample) and record in the Soil Fractionation logbook.

12.10 Transfer the soil that **did not** pass through the 60-mesh sieve to the pre-weighed vial labeled Coarse. Weigh the combined (vial + sample) and record in the Soil Fractionation logbook.

12.11 Digest soil fractions per US EPA SW846-3050 (SOP HN-MET-009).

12.12 LCS1 – Digest 1.0g of NIST 8704. True concentration = 150 mg/Kg

12.13 LCS2 – Digest 1.0g of NIST 2586. True concentration = 432 mg/Kg

12.14 MS/MSD – Spike 1.0g sample with 5mL of Metals Custom Standard 901. True concentration = 50 mg/Kg.

13) Troubleshooting

13.1 Refer to the appropriate digestion and/or analytical method for troubleshooting.

14) Data Acquisition

14.1 Record all necessary data in the applicable preparation logbook/excel spreadsheet.

14.2 Refer to the appropriate digestion and/or analytical method for data acquisition.

15) Calculation, and Data Reduction Requirements

15.1 Refer to the appropriate digestion and/or analytical method for data reduction procedures.

15.2 Calculate the percent total solids in the soil

$$\% \text{ Total Solids} = (DW/WW) \times 100$$

where: DW = Sample weight dried
WW = Sample weight as received

15.3 Analytical results for lead shall be based on dry weight.

15.4 Report analytical concentrations of lead in the fine and coarse fractions, separately.

15.5 Report total lead concentrations based upon the fine and coarse fractions adjusted for weight.

$$\text{Total Lead} = [(Conc_f \times W_f) + (Conc_c \times W_c)] / (W_f + W_c)$$

Where: $Conc_f$ = Lead Concentration in fine fraction
$Conc_c$ = Lead Concentration in coarse fraction
W_f = Total Weight of the fine fraction
W_c = Total Weight of the coarse fraction

16) Quality Control, Data Assessment and Corrective Action

16.1 Refer to the appropriate digestion and/or analytical method for data acquisition.

17) Data Records Management

17.1 All preparative data shall be stored both electronically and in hard copy. Hard copy documentation shall be maintained via logbooks for standard and chemical tracking, digestion logs, instrument maintenance, and instrument run logs. Hardcopy and electronic records shall be maintained for a period of no less than 10 years.

17.2 Refer to the appropriate digestion and/or analytical method for data and/or record management.

18) Quality Assurance and Quality Control

18.1 Logbooks must be reviewed by the department supervisor monthly.

18.2 Logbooks must be reviewed by the QA staff quarterly.

19) Contingencies for Handling Out of Control Data

19.1 When method required QC failures occur, in every case where sample data quality are affected, the source of the QC failure must be determined, corrected and sample reanalysis carried out whenever possible.

19.2 When affected sample analysis cannot be repeated due to limitations on sample availability, or if reanalysis can only be performed after expiration of a sample hold time, the reporting of data associated with failed QC must be appropriately flagged and narrated for the data user, so as to define what effect the error has upon the results reported.

19.3 All analysts must report sufficient comments in LIMS for failed QC associated with sample results, so that project management can further narrate and ensure data qualifiers (flags) are properly assigned. See SOP HN-QS-009, *Date Reduction, Review and Validation.*

20) Method Performance

20.1 N/A

21) Summary of Changes

Table 21.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
R03	7/1/12	CES	Formatting
R04	1/31/16	CES	Updated document revision and data retention criteria. Included QC samples (LCS1, LCS2, and MS/MSD)

22) References and Related Documents

22.1 Michigan Department of Environmental Quality Standard Operating Procedure 213, Revision 1, Effective 11/04.

22.2 ALS Environmental Quality Assurance Manual, Revision (most current)

METALS BY ICP-MS

EPA 200.8 / SW846 6020A

SOPID:	HN-MET-008	Rev. Number:	R11	Effective Date:	10/15/2017

Approved By: _____ Date: 9/21/17
Department Supervisor

Approved By: _____ Date: 9/21/17
QA Manager

Approved By: _____ Date: 9/21/17
Laboratory Director

Archival Date: _____ Doc Control ID#: _____ Editor: _____

PROCEDURAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR 24 ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

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1) Scope and Applicability

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of a large number of elements as either dissolved (aqueous only) or total metals.

1.2 This method is applicable to a variety of matrices including: drinking water, non-potable water, solid/chemical materials, and biological tissue.

1.3 ICP-MS has been applied to the determination of over 60 elements in various matrices. The method is applicable to analytical ranges of approximately 0.005 mg/L to 900 mg/L for aqueous matrices and 0.5 mg/kg to 900 mg/kg for solid matrices.

1.4 Method detection limits, quantitation limits, and linear ranges will vary with matrices, instrumentation, and operating conditions.

1.5 SW-846 Method 6020A is used to determine the analytes listed in Tables 20.1-A. This table lists more elements than the current version of Method 6020A. The additional elements are included based upon results of demonstrations of precision and accuracy and completion of method detection limit studies for aqueous and solid matrix.

1.6 Method 200.8 is used to determine the analytes listed in Table 20.1-B. This table lists more elements than the current version of Method 200.8. The additional elements are included based upon results of demonstrations of precision and accuracy and completion of method detection limit studies for aqueous matrix.

1.7 Internal standards are used for each analyte determined by ICP-MS. The internal standard mix used consists of ^{6}Li, ^{45}Sc, ^{89}Y, ^{115}In, ^{159}Tb, ^{165}Ho, and ^{209}Bi. ^{89}Y is used for analysis in helium gas mode.

2) Summary of Procedure

2.1 Prior to analysis, samples that require total ("acid-leachable") values must be digested using appropriate sample preparation methods as specified in SOP HN-MET-009 and HN-MET-010, *Metal Digestion in Solid and Aqueous Matrices for ICPMS.*

2.2 Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. Ions are produced by radio frequency inductively coupled plasma, entrained in the plasma gas, and introduced into a mass spectrometer. The ions are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3) Definitions

3.1 Laboratory Control Sample (LCS): An analyte-free matrix spiked with known concentrations of all target analytes. This is used to evaluate and document laboratory method performance.

3.2 Matrix: The component or substrate (e.g., surface water, groundwater, soil) which contains the analyte of interest.

3.3 Matrix Spike (MS): An aliquot of background sample spiked with a known concentrations of all target analytes. The spiking occurs prior to sample preparation

and analysis. A matrix spike is used to assess the bias of a method in a given sample matrix.

3.4 Matrix Spike Duplicate (MSD): A duplicate aliquot of the background sample spiked with a known concentrations of all target analytes. Spiking occurs prior to sample preparation and analysis. The MS/MSD pair are used to assess precision and bias of a method in a given sample matrix.

3.5 Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

3.6 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. The LOQ is also referred to as the method quantitation limit (MQL) or the reporting limit (RL).

3.7 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix-specific and may be laboratory-dependent.

3.8 Method Detection Limit (MDL) study: the procedure, as described in 40CFR part 136, for determining the LOD based on statistical analysis of 7 low-level replicate spikes. The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

3.9 Standard Curve: A plot of concentrations of known analyte standards versus the instrument response to the analyte.

3.10 Internal Standard: A known amount of standard added to a test portion of a sample and carried through the entire measurement process as a reference for evaluating and controlling the precision and bias of the analytical test method.

3.11 Linear Dynamic Range (LDR): The concentration range through which the instrument response is linear.

3.12 Low-Level Quality Control sample (LLQC): A clean matrix sample spiked at the MQL and carried through the entire preparation and analysis process.

3.13 Low-Level Initial Calibration Verification (LLICV): A sample spiked at the MQL, used to validate the lower end of the initial calibration.

3.14 Low-Level Continuing Calibration Verification (LLCCV): A sample spiked at the MQL and analyzed periodically throughout an analytical sequence, monitoring continued performance of the lower end of a calibration.

4) Health and Safety Warnings

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data

handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HN-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

5) Cautions

5.1 Routine preventative maintenance must be performed as scheduled and documented to assure optimum instrument performance. Typical routine maintenance includes inspection and replacement of sample delivery tubing. Maintenance performed shall be recorded in a dedicated instrument maintenance logbook. Refer to HN-EQ-004 for additional information.

6) Interferences

6.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z) as those being monitored. A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Isotope ratios should be established prior to the application of any corrections.

6.2 Isobaric molecular and double-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature [3,4]. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature [5], the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar^{35}Cl^+$ signal): corrected arsenic signal (using natural isotopes abundances for coefficient approximations) = (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal), (where the final term adjusts for any selenium contribution at 77 m/z). A listing of employed correction equations is included in section 21.10.

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes [6]).

6.3 The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent. This type of correction has been reported for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol de-solvation and/or mixed plasma has been shown to greatly reduce molecular interferences. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met.

6.4 Physical interferences can be associated with sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.04% (400 mg/L) are recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes. When completing analysis by Method 6020A, if the intensity level of an internal standard falls below 70 percent of the intensity of the calibration standard used for reference, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed. When completing analysis by Method 200.8 and the intensity of the internal standard is less than 60 percent or greater than 125 percent of the intensity of the calibration standard used for reference, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.

6.5 Memory interferences can occur when there are large concentration differences between samples or standards that are analyzed sequentially. Sample deposition on the sampler or skimmer cone, spray chamber design, and the type of nebulizer affects the extent of the memory interferences that are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.

7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HN-QS-009).

7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.

7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.

7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.

7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

7.5.1 Approving deviations and non-conformances

7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,

7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Aqueous samples shall be collected in 500 ml plastic containers and preserved to a pH of <2 with HNO_3.

8.2 Drinking water samples for the analysis of Lead and Copper, under the EPA Lead and Copper Rule, shall be collected as "first draw" aliquots, in 1L wide mouth, plastic containers and preserved to a pH of <2 with HNO_3.

8.3 Dissolved metal analyses shall be field filtered through a 0.45µ filter and preserved to a pH of <2 with HNO_3. Filtering should be completed in the field at time of sampling.

8.4 Sample pH should be verified at time of sample receipt and adjusted if necessary.

8.4.1 If adjusted at time of receipt, the sample shall be stored for a period of 24 hours after which the pH adjustment will be verified.

8.5 Soil samples should be collected in 4 oz wide mouth plastic containers.

8.6 Samples may be stored at room temperature. The holding time is six months for aqueous and solid matrices.

9) Equipment and Supplies

9.1 Inductively coupled plasma-mass spectrometer (Agilent 7500ce / Agilent 7800): Capable of providing resolution, better than or equal to 1.0 amu at 5% peak height. The system must have a mass range from at least 5 to 250 amu and a data system that allows for corrections of isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon/helium and a peristaltic pump for the sample solution is required.

9.2 Various Class A volumetric flasks: 10.0, 25, 50, 100, 250, etc.

9.3 Variable volume pipettes: 1.0 and 5.0 ml.

10) Standards and Reagents

10.1 Argon gas supply: High-purity grade (99.99%).

10.2 Helium gas supply: High-purity grade (99.99%).

10.3 Nitric acid, concentrated (trace metal grade)

10.4 Hydrochloric acid, concentrated (trace metal grade)

Note: Acids used in the preparation of standards and samples for ICP-MS must be of high purity. Re-distilled acids are recommended due to the high sensitivity of the instrumentation.

10.5 Diluent Solution

10.5.1 Prepare as a solution containing 5% HNO3 – 1% HCl.
10.5.2 Prepare fresh daily.

10.6 Stock Spike Standards:

10.6.1 Metals Mix standard w/ Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Sb, Se, Sr, Sn, Tl, V, and Zn @ 10 mg/L **and** Fe, K, Ca, Na, and Mg @ 1000 mg/L **and** B at 50 mg/L. (available from VHG ZALSLAB901-500 or equivalent)
10.6.2 Si, Th, Ti, and U Spike Stock @ 1000 ppm (available from Environmetal Express or equivalent)

10.6.2.1 Single Element Working Spike Th, Ti, U @ 10 mg/L and Si @ 50 mg/L.

10.6.2.1.1 Add 5 ml Th, Ti, U and 25 ml Si Stock to 300 ml DI water in a 500 ml volumetric flask.
10.6.2.1.2 Acidify with 10 ml Nitric and 5 ml Hydrochloric acid.
10.6.2.1.3 Bring to final volume with DI water.

10.6.3 Low-level Metals Mix Standard I w/ As, Ba, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Sr, Tl, U, and V @ 0.5 mg/L **and** Be and Cd @ 0.2 mg/L **and** Al, Li, and Zn @ 1.0 mg/L **and** B @ 2.0 mg/L **and** Fe @ 8.0 mg/L **and** Mg, K, and Na @ 20 mg/L **and** Ca @ 50 mg/L. (available from VHG ZALSLAB1103-100 or equivalent)
10.6.4 Low-level Metals Mix Standard II w/ Sn @ 0.2 mg/L **and** Sb, Mo, and Ti @ 0.5 mg/L. (available from VHG ZALSLAB1104-100 or equivalent)
10.6.5 Low-level Metals Mix Standard III w/ Th @ 0.5 mg/L and Si @ 100 mg/L.

10.7 Initial Calibration Stock Standards (available from SPEX or equivalent):

10.7.1 Stock 1: 20 mg/L – Ag, Al, As, Ba, Be, Cd, Co, Cu, Cr, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V, Zn,
10.7.2 Stock 2: 1,000 mg/L – B
10.7.3 Stock 3: 1,000 mg/L – Fe, K, Ca, Na, Mg
10.7.4 Stock 4: 1,000 mg/L _ Sr
10.7.5 Stock 5: 1,000 mg/L – Ti
10.7.6 Stock 6: 1,000 mg/L - Sn
10.7.7 Stock 7: 1,000 mg/L – Li
10.7.8 Stock 8: 1,000 mg/L - Si
10.7.9 Stability of stock standards shall be consistent with the manufacturer's expiration date.

10.8 Intermediate Stock Standard for B and Si @ 100 mg/L and Sr, Ti, Sn @ 10 mg/L and Li @ 50 mg/L:

10.8.1 Add approximately 40 mL of DI water to (3) 50 mL volumetric flasks. Acidify each using 2 mL Nitric acid and 0.5 mL Hydrochloric acid.
10.8.2 Quantitatively add 0.5 mL each of Stock 4, 5, and 6 (from Section 10.7) to first flask.
10.8.3 Quantitatively add 5.0 mL of Stock 2 and 8 (from Section 10.7) to the second flask.
10.8.4 Quantitatively add 2.5 mL of Stock 7 (from Section 10.7) to the third flask.
10.8.5 Bring each to a final volume of 50 ml with DI water.
10.8.6 The intermediate stock standard is stable for a period of 6 months. The expiration date may not exceed that of any parent solution.

10.9 Working Initial Calibration Standards:

10.9.1 Working Calibration Stock Standard

10.9.1.1 Add approximately 125 ml of DI water to a 200 ml Class A volumetric flask. Acidify with 8 ml Nitric acid and 2 ml Hydrochloric acid.
10.9.1.2 Add 10 ml of Stock 3 (Section 10.7.3), 10 ml of Sr, Ti, Sn, intermediate stock (Section 10.8.2), 5 ml of B, Si intermediate stock (Section 10.8.3), 2 ml of Li intermediate stock (section 10.8.4), and 5 ml of Stock 1 (Section 10.7.1).
10.9.1.3 Bring to a final volume of 200 ml with DI water.
10.9.1.4 The working standard must be replaced weekly and the expiration date may not exceed that of any parent solution.

10.9.2 Calibration Standards

10.9.2.1 Prepare, at a minimum, five (5) initial calibration standards from the Working Calibration Stock Standard (Section 10.9.1) as detailed in Table 10.9.2.

Table 10.9.2

Standard (Note 1)	Amount of Working Calibration Stock	Final Volume (Note 2)	Final Concentration
Level I	0 ml	50 ml	0 µg/L
Level II	1.0 mL of Level V	50 ml	0.2 µg/L
Level III	1.0 ml of Level VII	50 ml	2 µg/L
Level IV	2.5 ml of Level VII	50 ml	5 µg/L
Level V	5.0 ml of Level VII	50 ml	10 µg/L
Level VI	5 ml	50 ml	50 µg/L
Level VII	10 ml	50 ml	100 µg/L
Level VIII	20 ml	50 ml	200 µg/L

Note (1): Additional standards may be added to extend the calibration range.
Note (2): All standards must be adjusted to a final acid concentration of 4% HNO_3 and 1% HCl solution.

10.10 Stock Calibration Check Solutions (ICS):

10.10.1 ICS1: Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Se, Tl, U, V, Zn @ 10

mg/L. (available from SPEX)

10.10.2 ICS3: Ca, Fe, K, Mg, Na @ 200 mg/L. (available from SPEX)

10.10.3 ICS5: Mo, Sn, Sr, Ti @ 10 mg/L. (available from SPEX)

10.10.4 Boron and Si @ 1,000 mg/L. (available from Environmental Express or equivalent)

10.10.4.1 Boron and Si Working Solution @ 50 mg/L

10.10.4.1.1 Add approximately 40 ml of DI water to a 50 ml Class A volumetric flask. Acidify with 2 ml Nitric acid and 0.5 ml Hydrochloric acid.

10.10.4.1.2 Add 2.5 ml of the 1,000 mg/L Boron standard and 2.5 ml of the 1,000 mg/L Si standard (Section 10.10.4).

10.10.4.1.3 Bring to a final volume of 50 ml with DI water.

10.10.4.1.4 Solution is stable for a period of 6 months

10.10.5 Lithium and Thorium @ 1,000 mg/L. (available from Environmental Express or equivalent)

10.10.5.1 Lithium/Thorium Working Solution @ 10mg/L

10.10.5.1.1 Add approximately 40 ml of DI water to a 50 ml Class A volumetric flask. Acidify with 2 ml Nitric acid and 0.5 ml Hydrochloric acid.

10.10.5.1.2 Add 0.5 ml of the 1,000 mg/L Lithium/Thorium standard (section 10.10.5).

10.10.5.1.3 Bring to a final volume of 50 mL with DI water.

10.10.5.1.4 Solution is stable for a period of 6 months.

10.11 Initial Calibration Verification (ICV/CCV) Solution:

10.11.1 Working ICV/CCV Solution @ 80/8000/80/400 for CLP Method ICV only.

10.11.1.1 Add 500 µl ICS1 (Section10.10.1), 2 ml ICS3 (Section 10.10.2), 400 µl ICS5 (Section 10.10.3), 400 µl of boron/silica working solution (Section 10.10.4.1), and 400 µl Lithium/Thorium working solution (Section 10.10.5.1) to a 50 ml Class A volumetric flask.

10.11.1.2 Bring to volume with diluent solution (Section 10.5)

10.11.1.3 Prepare fresh daily.

10.11.2 The stock standard(s) for the ICV solution must be obtained from a second source supplier or, if purchased from the same supplier, be a different solution warrantied to be prepared from a different lot of parent constituents.

10.12 Low-Level Initial Calibration Verification solution (LLICV/CCV) spike @ MQL:

10.12.1 Add approximately 40 mL DI water to a 50 mL volumetric flask and acidify with 2 mL Nitric acid and 0.5 mL Hydrochloric acid.

10.12.2 Pipet 0.5 mL Low-Level Metals mix standard I (section 10.6.3) and 0.5 mL Low-Level Metals mix standard II (section 10.6.4)

10.12.3 Bring to volume with DI water.

10.12.4 Prepare fresh daily

10.13 Initial Calibration Blank (ICB):

10.13.1 Prepare reagent water with a 4% HNO_3 & 1% HCl content.

10.14 Interference Check Sample A (ICSA) Stock Standard – Available from SPEX: Cl @ 10,000 mg/L; C @ 2,000 mg/L; Al, Ca, Fe, K, Mg, Na, P, S @ 1,000 mg/L; Mo, Ti @ 20 mg/L.

10.15 Interference Check Sample A (ICSA) Working Standard

10.15.1 Add 2.5 ml of ICSA (Section 10.14) to a 50 ml Class A volumetric flask.
10.15.2 Dilute to 50 ml with diluent solution (Section 10.5).
10.15.3 Prepare weekly.

10.16 Interference Check Sample AB (ICSAB) Working Standard

10.16.1 Prepare same as CCV (Section 10.11.1) not bringing to final volume.
10.16.2 Add 2.5 ml ICSA (Section 10.14)
10.16.3 Dilute to 50 ml with diluent solution (Section 10.5).
10.16.4 Prepare weekly.

10.17 Linear Dynamic Range (LDR) Check Solution

10.17.1 Add 10 ml Stock Spike (Section 10.6.1 and 10.6.2) to a 50 ml Class A volumetric flask.
10.17.2 Bring to volume with diluent (Section 10.5).
10.17.3 This solution should be replaced weekly or if degradation is noted. The expiration date may not exceed that of any parent solution.

10.18 Continuing Calibration Blank:

10.18.1 Same as Section 10.13.

10.19 Continuing Calibration Verification:

10.19.1 Same as Section 10.11.

10.20 Low-Level Continuing Calibration Verification:

10.20.1 Same as Section 10.12.

10.21 Internal Standard Stock Standard:

10.21.1 Yttrium @ 1000 mg/L. Available from Environmental Express.
10.21.2 Multi-Element Mix containing Li, Sc, Y, In, Tb, Ho, and Bi @ 10 mg/L. Available from VHG Labs.

10.22 Internal Standard – Working Solution:

10.22.1 Add 5 ml of Multi-Element Mix (Section 10.21.2) and 500 µl of Y standard (Section 10.21.1) to a 50 ml Class A volumetric flask.
10.22.2 Bring to volume with diluent (Section 10.5).
10.22.3 This solution should be replaced if degradation is noted. The expiration date may not exceed that of any parent solution.

10.23 ICP-MS Tune Stock Solution:

10.23.1 Tuning solution containing 10 mg/L of Be, Mg, Co, In, Ba, Ce, Li, Rh, Tl, U, Y, and Pb.

10.24 ICP-MS Working Tune Solution @ 10 ppb:

10.24.1 Dilute 1 ml of the ICP-MS tune stock solution (Section 10.23.1) to 1 L.
10.24.2 Working tune solution must be replaced every 6 months or if degradation is noted. The expiration date of this solution may not exceed that of its parent.

10.25 Stock Spiking Solution:

Multi-element standards documented in Sections 10.6.1 and 10.6.2 shall be used for spiking.

10.25.1 Soil Spike:

10.25.1.1 A 500 µl volume of each spike solution is added to 0.5 gram of solid after transfer to the digestion vessel. Following digestion (HN-MET-009), the digestate is brought to a final volume of 50 ml. Theoretical spike value is the 100 mg/kg for the trace metals, 1000 mg/kg for Ca/Fe/Mg/Na/K, and 25 mg/kg for B and Si.

10.25.2 Water Spike:

10.25.2.1 A 500µl volume of spike solutions 10.6.1 and 10.6.2 is added to the 50.0 ml volume of aqueous sample after transfer to the digestion vessel. Following digestion (HN-MET-010), the digestate is brought to a final volume of 50.0 ml. Theoretical spike value is 0.1 mg/L for the trace metals, 10 mg/L for Ca/Fe/Mg/Na/K, and 0.5 mg/L for B and Si.

11) Method Calibration

11.1 Start-up Procedure

11.1.1 Visual check of instrument:

11.1.1.1 Inspect auto-sampler tubing; peristaltic pump tubing should be replaced daily.
11.1.1.2 Inspect sampling cone and skimmer cone for deposit build up; if build up is noticed, either clean or replace cone.
11.1.1.3 Verify argon gas flow; ensure there is 100 PSI coming into the instrument.
11.1.1.4 Check vacuum pressure and oil levels.
11.1.1.5 Check that the heat exchanger unit is turned on.
11.1.1.6 Record maintenance in routine maintenance logbook.

11.1.2 Turn plasma on and let the instrument stabilize for approximately 30-45 minutes.
11.1.3 During stabilization, verify basic instrument operating parameters. These parameters should be set at approximately:

11.1.3.1 RF power = 1500V
11.1.3.2 RF matching = 1.8V
11.1.3.3 Peristaltic Pump = 0.1 rps
11.1.3.4 S/C Temp = 2° C.

11.1.3.5 Small adjustments to the EM voltage and/or maintenance may be required to meet subsequent tuning specification. This may be done using the Autotune function in the software.

11.1.4 After instrument stabilization, perform an instrument tune using the ICP-MS Tune solution (Section 10.24). This is a preliminary tune to evaluate performance across the operating mass range of the instrument.

11.1.4.1 Analyze the ICP-MS tune solution in 5 replicates prior to the initial calibration.
11.1.4.2 Adjust mass calibration such that the unit mass falls within $\pm$ 0.1 amu of the expected value.
11.1.4.3 Acceptance Criteria:

11.1.4.3.1 Resolution should be ~ 0.75 amu at 5% peak height, and **must** be <0.90 amu.
11.1.4.3.2 Mass calibration must be +/- 0.1 amu from the true value.
11.1.4.3.3 Relative standard deviations (RSD) of absolute signals from the five replicates must be < 5% for all analytes.
11.1.4.3.4 Internal standard criteria are not applicable to the ICP-MS tune solution.

11.1.5 A P/A factor update shall be performed utilizing the 10ug/L standard incorporated in the initial calibration curve. This should be updated on a regular basis when a calibration curve begins to fail, a new calibration curve is used, and after instrument maintenance.
11.1.6 A five-point calibration (minimally) must be conducted daily utilizing a calibration blank and four calibration standards (Section 10.9.2).

11.1.6.1 All measurements must be based upon at least three integrations.
11.1.6.2 Reported values must use the average of the multiple integrations.
11.1.6.3 Results of the calibration blank must be < 3 times the current IDL for each element.
11.1.6.4 Internal standard criteria must be achieved for all analyses.

11.2 Initial Calibration Curve:

11.2.1 A linear regression (first order fit) of the instrument response versus the concentration of the standards is employed for subsequent quantitation. The instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:
y = instrument response (peak area)
a = slope of the line (coefficient of x)
x = concentration of the calibration standard
b = blank intercept

11.2.2 The analyst should not force the line through the origin, but have the intercept calculated from the five data points.
11.2.3 The regression calculation correlation coefficient (r) must be $\geq$ 0.998.

11.3 Initial Calibration Verification (ICV):

11.3.1 The initial calibration must be verified utilizing a second source calibration verification standard at a concentration below the mid-point of the calibration curve (Section 10.11).
11.3.2 The ICV must be run after each new initial calibration curve.
11.3.3 Must meet accuracy performance criteria of 90-110% as outlined in the applicable LIMS test code.
11.3.4 Internal standard criteria must be achieved for the ICV analysis.

11.4 Low-Level Initial Calibration Verification (LLICV):

11.4.1 The LLICV is analyzed at the laboratory MQL to verify the lower end of the initial calibration. (Section 10.12)
11.4.2 The LLICV must be run after each new initial calibration
11.4.3 Must meet accuracy performance criteria of 70-130% as outlined in the applicable LIMS test code.
11.4.4 Internal standard criteria must be achieved for the LLICV analysis.

11.5 Interference Check Solutions (ICS):

11.5.1 The ICS (Section 10.15 & 10.16) must be analyzed at the beginning of an analytical sequence and every 8 hours during the analytical run.
11.5.2 Must meet accuracy performance criteria of 80-120% as outlined in the applicable LIMS test code.
11.5.3 Internal standard criteria must be achieved for each ICS analysis.

11.6 Continuing Calibration Verification (CCV):

11.6.1 A same source standard must be analyzed at the beginning of each daily batch, after a maximum of 10 samples run (including the Method Blank, LCS, and MS/MSD), and at the end of the analytical run.
11.6.2 Must meet accuracy performance criteria of 90-110% as outlined in the applicable LIMS test code.
11.6.3 Internal standard criteria must be achieved for each CCV analysis.

11.7 Low-Level Continuing Calibration Verification (LLCCV):

11.7.1 A low-level sample (section 10.20) must be analyzed at the beginning of each daily sequence, after a maximum of 10 samples run (including QC), and at the end of the analytical sequence.
11.7.2 Must meet accuracy performance criteria of 70-130%, for samples of a similar concentration, as outlined in the applicable LIMS test code.
11.7.3 Internal standard criteria must be achieved for each LLCCV analysis.

12) Sample Preparation/Analysis

12.1 Digestion procedures are presented in the applicable sample preparation SOP (HN-MET-009 and HN-MET-010).

12.2 When internal standard response falls outside acceptance criteria (<70% for 6020A and <60% or >125% for 200.8), dilute the sample and reanalyze.

12.3 Typical Analytical Sequence:

12.3.1 Initial Calibration curve, minimum four standards and a blank

12.3.2 Initial Calibration Verification standards (once daily)
12.3.3 Initial Calibration Verification Blank (once daily)
12.3.4 Low-Level Initial Calibration Verification Standard (once daily)
12.3.5 Interference Check Sample A (ICSA)
12.3.6 Interference Check Sample AB (ICSAB)
12.3.7 Continuing Calibration Verification (CCV)
12.3.8 Low-Level Continuing Calibration Verification Standard (LLCCV)
12.3.9 Continuing Calibration Blank (CCB)
12.3.10 Method blank (one MB per preparation batch of 20 or less)
12.3.11 Laboratory Control Sample (one per preparation batch of 20 or less)
12.3.12 Client sample(s)
12.3.13 Matrix spike

12.3.13.1 For Method 200.8, prepare at a 10% frequency (one per every 10 samples)
12.3.13.2 For Method 6020A, prepare at a 5% frequency (one per preparation batch of 20 or less)

12.3.14 Matrix spike duplicate

12.3.14.1 For Method 200.8, prepare at a 10% frequency (one per every 10 samples)
12.3.14.2 For Method 6020A, prepare at a 5% frequency (one per preparation batch of 20 or less)

12.3.15 Continuing Calibration Verification Standard (CCV after every 10 samples)
12.3.16 Continuing Calibration Blank (CCB after every ten samples)
12.3.17 Low-Level Continuing Calibration Verification Standard (LLCCV after every 10 samples)
12.3.18 Client samples and batch QC samples (dilution test sample, PDS, MB, LCS and MS) – total of ten or less samples
12.3.19 Continuing Calibration Verification Standard (CCV at end of analytical sequence)
12.3.20 Continuing Calibration Blank (CCB at end of analytical sequence)
12.3.21 Low-Level Continuing Calibration Verification Standard (LLCCV at end of analytical sequence)

12.4 Dilution test:

12.4.1 If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank), an analysis of a fivefold dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected.

12.5 Post-Digestion Spike (PDS) Addition:

12.5.1 An analyte spike added to a portion of a prepared sample should fall within the laboratory derived acceptance criteria.
12.5.2 The spike addition should be based on the indigenous concentration of each element of interest in the sample.
12.5.3 If the spike is not recovered within the specified limits, the sample should be diluted and reanalyzed to compensate for the matrix effect.
12.5.4 Results must agree to within 10% of the original determination.

12.5.5 The use of a standard-addition analysis procedure may also be used if the dilution technique proves inconclusive.

12.5.6 Post Digestion Preparation:

12.5.6.1 To a 10 ml portion of digestion sample, add 100 µl of Metals mix standard I. (Section 10.6.1)

12.5.6.2 The theoretical spike is 100 ug/L for the trace metals, 10,000 ug/L for minerals, and 500 ug/L for Boron.

12.6 Method of Standard Additions (MSA):

12.6.1 When MS/MSD and PDS criteria are not met, the method of standard additions may be used to determine an accurate analyte level.

12.6.2 The MSA is an extension of the PDS where three PDS are performed on the same sample.

12.6.2.1 Ideally, the first PDS is spiked at approximately 50% of the estimated analyte concentration. The second PDS is spiked at ~100% and the third at ~150%.

12.6.3 The MSA analyte concentration is determined using linear regression using the four data points. An MS Excel spreadsheet calculation is employed to calculate results from MSA.

13) Troubleshooting

13.1 Refer to Agilent ICP-MS hardware manual for specific technical troubleshooting guidance.

14) Data Acquisition

14.1 Create a prep batch (as applicable) in LIMS.

14.2 The data acquired is transferred via Chemstation™ to LIMS electronically. Calculations are performed by Chemstation™ software and LIMS.

14.3 Analyst review of data is performed on the raw data and in LIMS prior to being validated. If results are above the analytes detectable range, it will be reported as "----------". Appropriate dilutions must be performed to generate reportable data.

15) Calculation, and Data Reduction Requirements

15.1 Calculation of Linear Regression Correlation Coefficient, r

$$r = \frac{\sum XY - \frac{\sum X \sum Y}{n}}{\sqrt{(\sum X^2 - \frac{(\sum X)^2}{n})(\sum Y^2 - \frac{(\sum Y)^2}{n})}}$$

Where:

X = individual values for independent variable
Y = individual values for dependent variable

n = number of pairs of data.
df = n-2

15.2 Calculation of the CCV % drift:

15.2.1 % Drift= [(Calculated conc - Theoretical conc) x 100] / Theoretical conc

15.3 The calibration curve versus sample response data produces the metal concentration in solution.

15.3.1 Equation for water samples:

$$Concentration(ug/L) = Sample\,\mathrm{Re}sponse(ug/L) x\ Dilution\ Factor\ (If\ Applicable)$$

15.3.2 Equation for soil samples (external calibration):

$$Concentration(ug/kg) = \frac{Sample\ Response(ug/L) xFV}{Weight\ of\ Sample\ (g)}\ x\ Dil.\ Factor\ (If\ Applicable)$$

Where:
FV = final volume of digestion, ml

15.3.3 If additional dilutions are used, the result must be multiplied by the total dilution factor.

15.4 QC Calculations: Calculate the percent recovery for various QC samples (MS, MSD, LCS) according to the following equations:

15.4.1 % Recovery, %R (for MS/MSD and LCS)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked)
SA = Spike Amount Added (mg/L or mg/kg).

15.4.2 % Recovery, %R (for standards and CCV)

$$\%R = \frac{(SSR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.4.3 % RPD (for precision or replication evaluation)

$$\%RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:

SR_1 = Sample result for replicate 1.
SR_2 = Sample result for replicate 2.

16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Instrument Detection Limit (IDL)

16.1.1 IDL determinations should be determined every three months and maintained with the instrument logbook.
16.1.2 IDL determinations are to be completed by averaging the standard deviations of seven measurements of a reagent blank, over a minimum of three non-sequential analytical runs.

16.2 Initial Calibration:

16.2.1 A calibration curve must be generated daily or whenever ICV/CCV fail to achieve acceptance criteria.
16.2.2 Acceptance Criteria:

16.2.2.1 Curve must be determined from a minimum of four standards and a calibration blank.
16.2.2.2 The regression coefficient "r" must be $\geq$0.998
16.2.2.3 All responses must be based upon the average of three integrations at a minimum

16.2.3 Curve Failure Corrective Action:

16.2.3.1 Check standards and/or perform maintenance as necessary to correct problem.
16.2.3.2 Process a new initial calibration curve

16.3 Initial Calibration Verification (ICV):

16.3.1 Perform daily after generation of the initial calibration curve.
16.3.2 Acceptance criteria:

16.3.2.1 Must meet accuracy performance criteria of 90-110% as outlined in the applicable LIMS test code.

16.3.3 ICV Failure Corrective Action:

16.3.3.1 Evaluate condition and age of standards being used and/or perform any needed system maintenance.
16.3.3.2 Reanalyze the ICV and /or generate a new calibration curve as necessary to achieve acceptable calibration criteria.

16.4 Low-Level Initial Calibration Verification (LLICV):

16.4.1 Perform daily after generation of the initial calibration curve.
16.4.2 Acceptance criteria:

16.4.2.1 Must meet accuracy performance criteria of 70-130% as outlined in the applicable LIMS test code.

16.4.3 LLICV Failure Corrective Action:

16.4.3.1 Evaluate condition and age of standards being used and/or perform any needed system maintenance.
16.4.3.2 Reprocess the LLICV and /or generate a new calibration curve as necessary to achieve acceptable calibration criteria.

16.5 Continuing Calibration Verification (CCV):

16.5.1 The CCV must be run prior to sample analysis, after every 10 samples (including QC samples), and at the end of the analytical sequence.
16.5.2 Acceptance Criteria:

16.5.2.1 Must meet accuracy performance criteria of 90-110% as outlined in the applicable LIMS test code.

16.5.3 CCV failure Corrective Action:

16.5.3.1 If the calibration does not meet the criteria, re-analyze the standard.
16.5.3.2 If subsequent analysis is outside of criteria, perform a new calibration curve.
16.5.3.3 All samples processed following the last acceptable CCV must be re-analyzed.
Note: If the CCV recovery exceeds the upper control limit and the associated sample result is non-detect, the sample may be reported.

16.6 Low-Level Continuing Calibration Verification (LLCCV):

16.6.1 The LLCCV must be run prior to sample analysis, after every 10 samples (including QC samples), and at the end of the analytical sequence.
16.6.2 Acceptance Criteria:

16.6.2.1 Must meet accuracy performance criteria of 70-130% for analytes of a similar concentration, as outlined in the applicable LIMS test code.

16.6.3 LLCCV failure Corrective Action:

16.6.3.1 If the calibration does not meet the criteria, re-analyze the standard.
16.6.3.2 If subsequent analysis remains outside of criteria, perform a new calibration curve.
16.6.3.3 All samples of similar concentration (<CCV), processed following the last acceptable LLCCV must be re-analyzed.
Note: If the LCS recovery exceeds the upper control limit and the associated sample result is non-detect, the sample may be reported.

16.7 Continuing Calibration Blank (CCB):

16.7.1 The calibration blank must be run prior to sample analysis, after every 10 samples (including QC samples), and at the end of the analytical sequence.

16.7.2 Acceptance Criteria:

16.7.2.1 All analytes are must be less than three times the IDL.

16.7.3 CCB failure Corrective Action:

16.7.3.1 If the calibration blank does not meet the criteria, re-analyze the blank.

16.7.3.2 If subsequent analysis falls outside of criteria, perform any necessary maintenance and perform a new calibration curve.

16.7.3.3 All samples processed following the last acceptable CCB must be re-analyzed.

Note: If the CCB concentration exceeds the upper control limit and the associated sample result is non-detect, the sample may be reported.

16.8 Linear Dynamic Range (LDR) Assessment

16.8.1 A LDR sample must be processed to assess linearity above the highest calibration standard.

16.8.2 Acceptance Criteria:

16.8.2.1 All analytes are must be within 10% of the true value of the LDR standard.

16.8.2.2 Sample concentrations greater than 90% of the LDR must be diluted and re-analyzed.

16.8.2.3 The LDR should be verified every 6 months (minimally) or whenever a modification in instrument hardware or operating conditions presents the potential for a change in the LDR.

16.8.3 LDR assessment failure Corrective Action:

16.8.3.1 If the LDR does not meet criteria for an analyte, no data for that analyte falling between the highest calibration standard and the LDR standard can be reported.

16.9 Blanks:

16.9.1 Rinse Blank(s)

16.9.1.1 Rinse blanks should be used to flush system components between blanks, standards, and samples.

16.9.1.2 Allow sufficient time to remove traces of the previous sample prior to new sample introduction.

16.9.1.3 Rinse blanks are not to be routinely run before QC samples. If carryover is an issue, rinse-out times may need to be addressed.

16.9.2 Calibration Blank(s)

16.9.2.1 See Section 16.7.

16.9.3 Method Blank(s)

16.9.3.1 A method blank must be processed with each batch of 20 or less samples of the same matrix and prepared on the same working shift.

16.9.3.2 Acceptance Criteria (Non-Potable Water and Soils):

16.9.3.2.1 All analytes of interest should be less than one half the PQL and must be less than the PQL.

16.9.3.2.2 Method blank values exceeding the PQL indicate laboratory/reagent contamination and should be considered suspect.

16.9.3.2.3 Method blank values exceeding the PQL may be considered useable if:

16.9.3.2.3.1 The blank analyte concentration is < 5% of the sample analyte concentration,

16.9.3.2.3.2 less than 5% of the regulatory limit,

16.9.3.2.3.3 or less than 3 times the MDL (whichever is greater),

16.9.3.2.3.4 All associated samples are appropriately qualified, and Project Management notification/approval is completed.

16.9.3.2.4 Other approved QA program requirements must be followed when the acceptable blank contamination specified in the approved QA project plan differs from the above.

16.9.3.3 Acceptance Criteria (Drinking Water):

16.9.3.3.1 All analytes of interest must be less than 2.2 times the MDL.

16.9.3.3.2 Method blank values exceeding the MDL may indicate laboratory/reagent contamination and should be considered suspect.

16.9.3.3.3 Method blank values exceeding 2.2 times the MDL may be considered useable if the blank concentration is <10% of the sample analyte concentration, and the sample is appropriately narrated.

16.9.3.4 Corrective Action:

16.9.3.4.1 If the method blank results do not meet the acceptance criteria above, then the laboratory must take corrective action to locate and reduce the source of the contamination.

16.9.3.4.2 All samples associated with the contaminated method blank must be reprocessed.

Note: If the MBLK concentration exceeds the upper control limit and the associated sample result is non-detect, the sample may be reported. **This note is not applicable to drinking water samples.**

16.9.3.4.3 If samples cannot be reprocessed due to insufficient sample volume, a non-conformance must be documented in the data checklist for the analytical run. This must provide sufficient detail for project narration and to ensure all appropriate data flags are entered into LIMS.

16.9.3.4.4 Data reported with an associated contaminated method

blank must be flagged with a "B".

16.10 Laboratory Control Sample (LCS):

16.10.1 The LCS must be processed with each batch of 20 or less samples of the same matrix and processed on the same shift.

16.10.2 Acceptance Criteria:

16.10.2.1 Must meet accuracy performance criteria as outlined in the applicable LIMS test code.

16.10.3 LCS Corrective Action:

16.10.3.1 If the LCS recovery does not meet acceptance criteria, the sample batch must be reprocessed.

Note: If the LCS recovery exceeds the upper control limit and the associated sample result is non-detect, the sample may be reported. **This note is not applicable to drinking water samples.**

16.10.3.2 If samples cannot be reprocessed due to insufficient sample volume, a non-conformance must be documented in the data checklist for the analytical run. This must provide sufficient detail for project narration and to ensure all appropriate data flags are entered into LIMS.

16.10.3.3 Data reported with a failed LCS must be flagged and narrated as to potential bias characteristics.

16.11 Low-level Quality Control Sample (LLQC):

16.11.1 The LLQC must be processed quarterly.

16.11.2 Acceptance Criteria:

16.11.2.1 Must meet accuracy performance criteria of 70-130% as outlined in the applicable LIMS test code.

16.11.3 LLQC Corrective Action:

16.11.3.1 If the LLQC recovery does not meet acceptance criteria, investigate the cause of the failure.

16.11.3.2 Reprocess the LLQC once the cause of the failure has been identified and corrected.

16.11.3.3 If a cause cannot be identified and corrected, spike LLQC at a higher concentration, process, and adjust PQLs accordingly.

16.12 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

16.12.1 A MS/MSD pair must be processed at a 10% frequency for Method 200.8 and at a 5% frequency for Method 6020A. MS/MSD samples must be of the same matrix and processed during the same working shift.

16.12.2 Acceptance Criteria:

16.12.2.1 Must meet accuracy and precision performance criteria as outlined in the applicable LIMS test code.

16.12.2.2 Recovery values should not be evaluated if the spike concentration is less than 25% of the parent concentration.

16.12.3 MS/MSD Corrective Action:

16.12.3.1 If the MS/MSD pair generates recovery values outside acceptance criteria, the deviation may be due to matrix effects. The LCS, internal standard recoveries, and calibration results must all be evaluated in order to determine if matrix interference is present. (Note that the MS/MSD are used to evaluate the matrix effect, not to control the analytical process.) If both the MS/MSD fall outside accuracy criteria for the same analyte, a matrix effect is suspected, assuming the LCS achieves accuracy criteria, and all internal standard recoveries are consistent.

As an example, if the matrix spikes exhibit low recovery but good precision, laboratory control samples exhibit acceptable accuracy, and internal standard recovery is consistent, the presence of matrix interference is probable.

16.12.3.2 If the MS/MSD pair generates inconsistent recovery values and/or suspect LCS values are present, laboratory error (and not matrix inference) is suspected.

As an example, if precision between the MS/MSD pair is poor and the LCS presents divergent results, the presence of laboratory error is probable.

16.12.3.3 If the MS/MSD fails acceptance criteria, the data must be evaluated for error or possible matrix effect.

16.12.3.4 If laboratory error is indicated, all associated samples must be reprocessed. If samples cannot be reprocessed due to limited sample volume or other similar circumstances, all reported values must be qualified and narrated as to potential bias or usability.

16.12.3.5 If matrix interference is indicated, associated samples may be reported with appropriate qualification and narration.

16.12.3.6 A non-conformance must be documented in the data checklist for either scenario and must contain sufficient detail for project narration and to ensure all appropriate data qualifiers have been entered into LIMS.

16.13 Internal Standards (IS):

16.13.1 Internal standards must be added to all samples with the exception of the ICPMS tuning solution. We utilize an automatic internal standard introduction system via a peristaltic pump.

16.13.2 Acceptance Criteria:

16.13.2.1 For samples processed according to USEPA 6020A, the IS results must be >70% of the original response in the initial calibration.

16.13.2.2 For samples processed according to USEPA 200.8, the IS results must fall between 60%-125% of the original response in the initial calibration.

16.13.2.3 Analytical results associated with IS failures may not be reported.

16.13.3 IS failure corrective action:

16.13.3.1 If criteria are not met, the cause of the problem must be determined, corrected, and the samples re-analyzed.
16.13.3.2 The sample must undergo a five-fold (1+4) dilution to alleviate potential matrix interference. Note: Greater dilutions may be necessary for samples contributing significant matrix interference.
16.13.3.3 Samples undergoing a necessary dilution due to IS failure must be notated as such if the target analyte concentration falls below the reporting limit.
16.13.3.4 If samples cannot be re-analyzed, all associated results must be qualified as "Unusable".

16.14 Reported Analyte Concentration

16.14.1 Reported concentrations for applicable analytes must be reported from the least dilute analysis that achieves all required quality control parameters.

16.15 Interference Check Solution:

16.15.1 The interference check solutions must be processed at the beginning of each analytical sequence and every 8 hours during an analytical run.
16.15.2 Acceptance Criteria:

16.15.2.1 Must meet accuracy performance criteria as outlined in the applicable LIMS test code.

16.15.2.2 All internal standard criteria must be achieved for the interference check solution analysis.

16.15.3 Interference Check Solution Failure

16.15.3.1 All samples associated with a failure of the ICS must be reprocessed.
16.15.3.2 If samples cannot be re-analyzed, all sample results must be qualified as unusable.

16.16 Dilution Test Check

16.16.1 If the sample analyte concentration is within the linear dynamic range and sufficiently high (>100 times the reagent blank), a sample dilution test should be completed at a five-fold dilution.
16.16.2 Acceptance Criteria

16.16.2.1 Must meet precision performance criteria as outlined in the applicable LIMS test code.

16.16.3 Dilution Test Failure

16.16.3.1 In the event of a dilution test failure, the sample must be closely inspected for indications of matrix interference.
16.16.3.2 A post digestion spike or standard addition should be completed on the failed sample to verify matrix interference.

16.17 Post Digestion spike requirements

16.17.1 One post digestion spike (PDS) must be completed for each batch of $\leq$ 20

samples.

16.17.2 The PDS should be spiked at the same level as the MS/MSD.

16.17.3 Acceptance Criteria

16.17.3.1 Must meet accuracy performance criteria as outlined in the applicable LIMS test code.

16.17.4 PDS Failure

16.17.4.1 If the spike is not recovered within the recommended limits, the sample must be diluted and reanalyzed.

16.17.4.2 The results of the diluted re-analysis must agree within ± 10% of the original determination.

16.17.4.3 If the PDS fails the various acceptance criteria, the sample should be processed using standard additions as detailed in Section 12.6.

16.18 Deviations and non-conforming events must be documented using a Nonconformance Corrective Action Report (NCAR) or as an Exception Report item on the laboratory review checklist. For mandatory QC failures (e.g. LCS), the NCAR must be submitted to the QA Manager via the NCAR database.

17) Data Records Management

17.1 All data is stored both electronically and hard copy for 12 years.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard tracking, analyst must attempt to use one lot of reagents and standards with each batch.

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section. "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.5 The effective date of this SOP is the date in the header or last signature date, whichever is most recent.

17.6 Logbooks must be reviewed monthly by the department supervisor.

17.7 Logbooks must be reviewed quarterly by the QA Staff.

18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When affected sample analysis cannot be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

19) Method Performance

19.1 Demonstration of Proficiency:

19.1.1 Initial Demonstration of Proficiency

19.1.1.1 The laboratory must determine linear dynamic range, method detection limits, and evaluation of quality control samples prior to sample analysis by this procedure.

19.1.2 Routine Demonstration of Proficiency

19.1.2.1 Each analyst must demonstrate initial proficiency with sample preparation and/or analytical determination by generating 4 sets of data of acceptable accuracy and precision for target analytes in a clean matrix.

19.1.2.2 Each analyst must demonstrate ongoing proficiency annually with each sample preparation and/or analytical determination method by generating 4 sets of data of acceptable accuracy and precision for target analytes in a clean matrix or by passing performance in approved PT evaluations.

19.2 Method Detection Limits (MDLs) must be determined on an annual basis (at minimum) or whenever major modifications are performed on instrumentation (ex: change detector, auto-sampler, etc.).

19.3 On-going laboratory performance must be documented via performance evaluation studies and must be completed approximately every 6 months.

20) Summary of Changes

Table 20.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
R06	9/1/12	CES	Sec. 12.3.11 removed; Sec. 16.6.3.3 (<CCV) added; Sec. 16.11.3.1,2,3 amended; removed Sec. Heading 16.12.4
R07	10/1/13	CES	Formatting; Change hold time of lab-filtered samples from 16 hours to 24 hours.
R08	1/15/16	CES	Review Frequency and Data Storage requirement. Update Internal Standard Criteria for 21.7 - 21.8. Removal of ORS Method.
R09	9/15/16	CES	Section 10.14 updated to include Phosphorous
R09	9/15/16	CES	Section 16 updated to include process of reporting non-detect data for samples when Quality Control criteria exceeds the upper limit.
R10	12/15/16	CES	Added interference correction equations.
R11	10/15/17	CES	Removed cover page graphics

R11	10/15/17	CES	Included sampling guidance for Pb and Cu Rule samples.
R11	10/15/17	CES	Included MBLK evaluation criteria for drinking water samples.
R11	10/15/17	CES	Included Thorium and Uranium as measured analytes.
R11	10/15/17	CES	Included record retention criteria for

21) References and Related Documents

21.1 Environmental Protection Agency, "Method 6020A Inductively Coupled Plasma Mass Spectrometry", Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Revision 1, February 2007.

21.2 U.S. Environmental Protection Agency, "Method 200.8, Inductively Coupled Plasma – Mass Spectrometry," Methods for Chemical Analysis of Water and Wastes, Revision 5.4, 1994.

21.3 ALS Environmental Quality Assurance Manual, Revision (most current)

21.4 Table 20.1-A - ICP-MS Analyte Listing for SW 846-6020A

21.5 Table 20.1-B - ICP-MS Analyte Listing for Method 200.8

21.6 Table 20.2 - LCS Acceptance Criteria

21.7 Table 20.3-A - Internal Standard Criteria for CLP SW 846-6020A

21.8 Table 20.3-B - Internal Standard Criteria for CLP Method 200.8

21.9 Table 20.4 - Calibration and QC Summary

21.10 Interference Correction Equations

Table 20.1-A

Analyte List: SW 846-6020A

Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lithium	(Li)	7439-93-2
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silicon	(Si)	7440-21-3
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Thallium	(Tl)	7440-28-0
Thorium	(Th)	7440-29-1
Tin	(Sn)	7440-31-5
Titanium	(Ti)	7440-32-6
Uranium	(U)	7440-61-1
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

(Additional analytes may be added based upon appropriate performance data.)

Table 20.1-B

Analyte List: Method 200.8

Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lithium	(Li)	7439-93-2
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silicon	(Si)	7440-21-3
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Thallium	(Tl)	7440-28-0
Thorium	(Th)	7440-29-1
Tin	(Sn)	7440-31-5
Titanium	(Ti)	7440-32-6
Uranium	(U)	7440-61-1
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

(Additional analytes may be added based upon appropriate performance data.)

TABLE 20.2 - LCS ACCEPTANCE CRITERIA FOR METALS ANALYSIS BY ICP/MS

Analyte	Water Spike Amt, mg/L	6020A Water Lower %R Limit	6020A Water Upper %R Limit	200.8 Water Lower % R Limit	200.8 Water Upper % R Limit	Soil Spike Amt, mg/Kg	Soil Lower % R Limit	Soil upper % R Limit
Aluminum	0.1	80	120	85.0	115	5	80	120
Antimony	0.1	80	120	85.0	115	5	80	120
Arsenic	0.1	80	120	85.0	115	5	80	120
Barium	0.1	80	120	85.0	115	5	80	120
Beryllium	0.1	80	120	85.0	115	5	80	120
Boron	0.5	80	120	85.0	115	25	80	120
Cadmium	0.1	80	120	85.0	115	5	80	120
Calcium	10.0	80	120	85.0	115	500	80	120
Chromium	0.1	80	120	85.0	115	5	80	120
Cobalt	0.1	80	120	85.0	115	5	80	120
Copper	0.1	80	120	85.0	115	5	80	120
Iron	10.0	80	120	85.0	115	500	80	120
Lead	0.1	80	120	85.0	115	5	80	120
Lithium	0.1	80	120	85.0	115	5	80	120
Potassium	10.0	80	120	85.0	115	500	80	120
Magnesium	10.0	80	120	85.0	115	500	80	120
Manganese	0.1	80	120	85.0	115	5	80	120
Molybdenum	0.1	80	120	85.0	115	5	80	120
Nickel	0.1	80	120	85.0	115	5	80	120
Selenium	0.1	80	120	85.0	115	5	80	120
Silicon	10	80	120	85.0	115	500	80	120
Silver	0.1	80	120	85.0	115	5	80	120
Sodium	10.0	80	120	85.0	115	500	80	120
Strontium	0.1	80	120	85.0	115	5	80	120
Thallium	0.1	80	120	85.0	115	5	80	120
Tin	0.1	80	120	85.0	115	5	80	120
Titanium	0.1	80	120	85.0	115	5	80	120
Thorium	0.1	80	120	85.0	115	5	80	120
Uranium	0.1	80	120	85.0	115	5	80	120
Vanadium	0.1	80	120	85.0	115	5	80	120
Zinc	0.1	80	120	85.0	115	5	80	120